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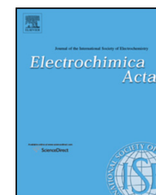

Current-Sensing Atomic Force Microscopic Study of Doping Level Distribution in Doped Poly[2,2'-Bithiophene]

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ABSTRACT

Current-sensing atomic force microscopy (CS-AFM) was used to study the doping level distribution in electrochemically doped poly[2,2'-bithiophene] under a controlled atmosphere (glove box) to preserve the doping level during the measurements. The resulting nanoscale conductivity distribution patterns were compared with those obtained with undoped polymer. The results were analyzed using the model developed by us earlier that the nanoscale morphology of such materials involves polymer grains with more crystalline cores and more disordered periphery. It turned out that while for the undoped polymer the crystalline cores were more conducting, the doped polymer featured more conducting periphery as compared to the grain cores. The results demonstrate that doping ions and solvent penetrate the polymer material non-uniformly and can more easily enter more disordered portions of the materials located at the periphery of the polymer grains. These results demonstrate the importance of structural factors for applications that require different levels of the material conductivity. In particular, more ordered materials look more suitable for such applications as molecular electronics and solar cells, which require low conducting/semiconducting materials with high carrier mobility. At the same time, for applications that require high levels of electronic conductivity, such as charge storage and various conducting coatings, less ordered polymer films would be preferred.

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1. Introduction

One of the most important and intriguing features of electron-conducting polymers is their ability to be doped either chemically or electrochemically. Doping is a complex process that normally involves oxidation or reduction of the polymer chains accompanied by the penetration of the doping ions and solvent into the polymer matrix. Despite numerous studies of the mechanism of the polymer doping, it is still unclear if this process occurs homogeneously or not, especially on the nanoscale, and, if the latter, what is the origin of the inhomogeneity and what are the preferred routes of the doping-ion penetration.

In our previous works [1–8] we have studied in detail the nanoscale inhomogeneity of electropolymerized electron-conducting polymers using atomic-force microscopy and its extensions, current-sensing AFM (CS-AFM) and phase imaging (PI). Typically, doping results in an increase in the polymer conductivity. This fact can be used to study the distribution of the doping level in such materials by means of nanoscale imaging of the material conductivity using CS-AFM [4,9–21]. Such imaging can be performed simultaneously with regular AFM imaging thus allowing one to correlate the doping level distribution with the polymer morphology. Using phase imaging, one can characterize the variations in the sample crystallinity and/or density, again, in relation to the polymer morphology [5–8,19,22,23]. Using these approaches, we have shown that the nanoscale structure of electrochemically synthesized polymers is fairly complex and non-homogeneous. In particular [4,5,19], the polymer grains were found to be comprised of material with different crystallinity/density and molecular weight (MW). More crystalline/dense domains were found in the cores of the polymer grain, whereas more disordered, lower MW fractions were located at the grain periphery. The distribution of the conductivity and thus the doping level was also characterized [4,19]. It was found that, for undoped samples, the conducting areas were again located at the cores of the polymer grains. This could be rationalized in terms, for instance, of trapping of doping charge introduced during the electropolymerization process, and/or by higher conductivity and lower oxidation potential of the more crystalline polymer fractions with higher MW [24–28].

However, these results were obtained only for as-grown samples, which were undoped and relatively low-conducting. It was of interest to characterize the distribution of the doping level in highly conductive doped polymer samples and compare such distribution with that found in undoped samples. This is the purpose of this work. We chose to use CS-AFM for this task. Although

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CS-AFM is a contact-mode technique and thus is potentially more destructive for the samples, it is preferred over other possible techniques such is Kelvin probe force microscopy (KFM) [29] since doping results in much more pronounced changes in the materials conductivity as compared to the work function. Moreover, although performed in tapping mode and thus potentially less destructive, KFM measurements are more susceptible towards various experimental factors [30] such as tip and sample surface contamination, residual moisture and solvent accumulation at the sample surface, variations in the work functions between different tips and therefore from one experiment to another, all of which make the KFM technique considerably less reliable for our task. In our earlier study [4], we found that the conducting polymer sample are sufficiently robust for reliable and reproducible imaging in the contact mode, including CS-AFM imaging, provided that tips with low spring constants and low imaging forces are used. The usage of doped diamond rather than metal coated tip was also found to be essential. Furthermore, we always checked for the sample damage by zooming out after the imaging over a certain area. If the surface were damaged, the damaged areas would have been easily observed due to their specific size and rectangular shape.

Normally, doped polymers, especially those with relatively high anodic redox potential such as poly[2,2'-bithiophene] used in this work, rapidly lose their conductivity and become undoped due to interaction with atmospheric oxygen and moisture. To preserve the conductivity and the doping level and avoid the spontaneous undoping, all the AFM imaging in this work was performed in a controlled atmosphere inside an argon-filled glove box. The samples were prepared and doped in the same glove box and thus were never exposed to ambient conditions.

2. Experimental

2.1. Preparation of polymer samples

A set of poly [2,2'-bithiophene] (PBT) samples were prepared by galvanostatic electropolymerization. The substrate in all cases was highly oriented pyrolytic graphite (HOPG) (NTMDT, ZYB quality). All PBT films were produced from a 0.005 M solution of 2,2'-bithiophene in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. 2,2'-Bithiophene (Aldrich) was purified through vacuum sublimation and tetrabutylammonium hexafluorophosphate (Aldrich, 98% purity) was used as received. Acetonitrile was purified using an SPS-400-5 solvent purification system (Innovative Technology) using columns packed with activated alumina and copper catalysts. The water content was less than 10 ppm. A Princeton Applied Research (PAR) Model 263A potentiostat/galvanostat controlled with version 2.8 Corrware/Corrview electrochemistry software (Scribner) was utilized. The monomer and supporting electrolyte salt were stored in vacuum desiccators over silica gel to prevent moisture accumulation.

Silver pseudo-reference electrodes (E = +0.05 vs SCE) and platinum counter electrodes were used. To improve stability and consistency, between measurements the reference electrode was stored in a solution of supporting electrolyte of the same concentration as during measurements. All potentials were measured and are presented with respect to this reference electrode.

The AFM images presented in this paper are typical ones selected from at least three independently prepared samples and from at least three different areas of the sample.

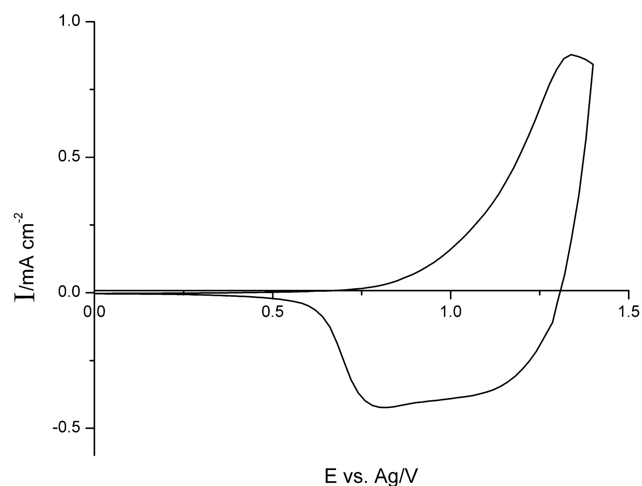

Fig. 1. A typical cyclic voltammogram for PBT polymer samples prepared by galvanostatic deposition onto a highly oriented pyrolytic graphite (HOPG) substrate. The scan rate was 100 mV s^{-1}.

2.2. Polymer film deposition and characterization

The electropolymerization was performed using a specially designed three-electrode Teflon cell mounted on top of the HOPG working electrode (the electrode surface area exposed to the solution was 0.28 cm^2) inside a glove box containing an argon atmosphere. All samples were prepared under galvanostatic conditions at a current density of 1 mA cm^{-2} for 50 s. After the deposition, the PBT films were reduced in the synthesis solution at a potential of 0.0 V (vs the Ag pseudo-reference electrode) for 100 s in order to convert them into a neutral/undoped state. The samples were then rinsed three times with pure acetonitrile in the apparatus. After rinsing, the synthesis solution was replaced with a 0.1 M solution of $TBAPF_6$ in acetonitrile without the monomer. A cyclic voltammogram typical of polymer samples prepared in this way is shown in Fig. 1.

The samples for AFM imaging were then anodically doped by ramping the potential at a scan rate of 100 mV s^{-1} from 0.0 V to +1.2 V, that is, slightly negative of the principal anodic doping peak, and then keeping the electrodes at that potential for 30 s. After doping, the samples were rinsed again three times with pure acetonitrile and dried at room temperature for at least 3 days to prevent the effect of residual solvent on the measurements. In addition to the doped samples, a non-doped PBT sample was also made under the same conditions. The thicknesses of all films presented in this work were determined to be ca. 90 nm. All manipulations were performed in the glove box under a controlled atmosphere.

2.3. AFM measurements of films

The atomic force microscopy (AFM) images were obtained using a Multimode atomic force microscope (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco) and a CS-AFM extension module (Veeco). The AFM imaging was performed in the same glove box containing an argon atmosphere as the sample preparation without any exposure of the films to ambient conditions.

The CS-AFM measurements were acquired in the contact mode using CDT-CONTR conducting diamond coated AFM probes (Nanosensors, force constant 0.2 N/m) at various bias levels applied between the sample and the conducting AFM tip. The bias values presented in this work correspond to current flowing from the sample to the tip, that is, at positive bias values, areas of higher

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